Quantitative Relation of Crystallinity and Crystallite's Size to Mechanical Properties of Semi-crystalline Polymers: Application to HDPE

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Abstract

Mechanical properties of semi-crystalline polymers can be determined by the material structures such as degree of the crystallinity and crystallite size. This paper presents quantitative relations of the crystallinity and the crystallite size to the mechanical properties of semi-crystalline polymers. Quantification of the complex relationship can be made through neural networks. The predictions by trained neural networks can be easily made for the effects of the crystallinity and the crystallite size on the mechanical properties of the high-density polyethylene.

1. Introduction

In semi-crystalline polymers, the degree of crystallinity, that is the morphology of the crystalline and amorphous regions, and the size of the crystallites have profound effects upon the mechanical properties of the polymers. In the polymer science and engineering, it is important to obtain descriptive models of the relationships between those material structures and the mechanical properties in assessing the characteristics of the polymer processing. The purpose of this study is to obtain such quantitative correlation between the material structures and the mechanical properties.

In polymer processing, the semi-crystalline polymers are melted in order to form them into the usable shapes. The polymers will crystallize to some extent when the molten polymers are cooled below the equilibrium melting temperature. There are many factors that can affect the material structures during which crystallization occurs such as cooling rate and deformation. In studies of Janeschitz-kriegl[1], cross-sections through polypropylene samples were observed after running the Differential Scanning Calorimetry (DSC) experiments at different cooling rates, that is 5 and 50 °C/min. Under these quiescent conditions, chain folding occurs rapidly in all directions, leading to a spherical structure. It was found that the average size of the spherulites is much smaller with the higher cooling condition. The small size of spherulites gives good mechanical properties while polymer materials are brittle when they have large spherulites. Sharples[2] also reported yield stress in Nylon66 varies according to the size of the spherulite. It was observed the yield stress increases when the size of spherulite decreases. This can be simply explained by the good "packing" of the molecular chain. However, increasing cooling rate may decrease the degree of the crystallinity in polymer materials. This may cause the poor performance of the semi-crystalline polymer on the mechanical properties.

In this study, the conventional multi-layer feedforward neural network is used to capture the qualitative relationships between the material structures and the mechanical properties. The modeling of the neural networks was omitted and more details can be seen in Leephakpreeda[3,4].

2 Experiment

2.1 Materials and preparation of samples

The pellets of High Density Polyethylene (HDPE) were obtained from Thai Petrochemical Industry Public Co., Ltd. Its commercial designation is Polene V1160. The pelletized samples were dried in a vacuum oven for 8 hours at 100 °C before filling up them into a stainless-steel mold with a size 150 x 200 x 3 mm^3 as shown in Fig. 1. Compression molding was performed by free heating the pelletized sample to the temperature about 150 °C for 10 minutes.

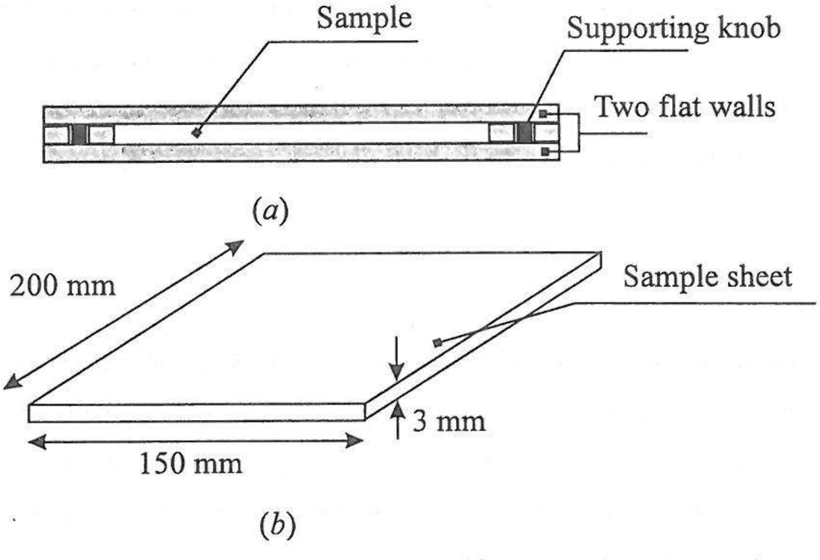

Fig. 1 Experimental for cooling a molten sample contained (a) Cross-sectional compression mold (b) Sample sheet for testing.

In Fig. 1 (a), the supporting knobs are used for not only stabilizing the compression mold but also absorbing applied load. The molten samples inside the compression mold were then quenched by the water at five various temperatures of 3 °C, 25 °C, 40 °C, 45 °C and 50 °C. Five sample sheets with different cooling conditions were used in order to determine the crystallinity, the size of the spherulites, the modulus of the elasticity and the impact strength.

2.2 Differential Scanning Calorimetry (DSC)

Measurements of the crystallinity were made with Perkin Elmer-7s. Samples were heated at a rate of 10 °C/min from the room temperature in a nitrogen atmosphere to temperature 170 °C. The endothermic enthalpy occurring during melting of the samples was observed in order to determine the degree of the crystalliniity.

2.3 X-ray deffraction

The X-ray diffraction technique was used to estimate the mean crystallite's size of the samples. The instrument MAX-2000 RIGOKU with 40-KVcopper-k-alpha source was used in order to obtain Wide Angle X-ray Diffractographs (WAXD) where the intensity of X-ray scattering is plotted against the diffraction angle.

2.4 Mechanical Property studies

The dumbbell shaped specimens of size 25 x 100 x 3 mm^3 with the gauge length 35 mm and width 7 mm were prepared to test modulus of elasticity which was measured by Lloyd instrument LR™ 30K ASTM standard. The rectangular samples with 10 x 50 x 3 mm^3 with V-notch were prepared for the impact strength testing. The equipment was used to be Yasuda™ 258-PC Tester ASTM Izod system. Mechanical-property testing was performed around the room temperature 25 °C.

3 Determination of the degree of the crystallinity

In the thermal analysis, the degree of the crystallinty α of the semi-crystalline polymer can be determined according to the following equation

$$\alpha = \frac{\Delta H}{\Delta H_{\infty}} \tag{1}$$

where ΔH is the actual heat of the fusion of a semi-crystalline polymer which can be determined from a measurement of the area under the DSC thermogram and ΔH_{∞} is the ultimate heat of the fusion of the semi-crystalline polymer, e.g. 179.79 kJ/kg for HDPE[4].

4 Determination of the size of the crystallites

It is widely known that the semi-crystalline polymers contain the crystalline and amorphous phases. The presence of such an imperfection may give rise to the broadening of any diffraction patterns. With the X-ray diffraction method[5], the broading of the diffraction maxima can be caused by the crystallites which have a finite size. The crystallite's size can be estimated form the degree of the broading of the maximum intensity in the diffraction. Let's denote a mean dimension normal to the (hkl) planes as D_{hkl}. The broading of the X-ray diffraction peak due to the size effect is given by

$$\delta\Re = \frac{1}{D_{hkl}} \tag{2}$$

where $\delta\Re$ is the deference of the diffraction peak at half-height and $\Re$ is defined as follows.

$$\Re = (2/\lambda)\sin\phi \tag{3}$$

where λ is the wavelength of the X-ray light and ϕ is the diffraction angle.

5 Determination of modulus of elasticity

The region of the gauge length is where tensile properties are measured. The modulus of Elasticity is defined as

$$E = \frac{\sigma}{\varepsilon} \tag{4}$$

where σ and ε are the stress and strain which occur during the test.

Note that very large changes in modulus can increase the extent of the crystallinity[6]. Therefore, the modulus of elasticity is determined at 5% of strain where the effect of stress-induced crystallization can be negligible.

6. Results and Discussions

The sample preparation in section 2.1 allows us to cool the HDPE sample sheets at the various cooling rates such that the extend of crystallinity and the size of spherulties can be varied. With the DSC experiments and the X-Ray diffraction method as mentioned above, Table 1 shows the amount of the crystallinity and the mean size of spherulites at the different quenching temperatures. The low quenching temperature can induce the high cooling rate inside the sample, vice versa. To get more clearly understanding, the cooling rate influence the amount of crystallinity and the size of the spherulites as graphically shown in Fig. 2 and 3. It should be noted that the percentage of crystallinity of samples quenched at 50 °C is considered to be 100% in this discussion since the value of ΔH is maximum.

Table 1 Crystallinity and spherulite size of HDPE at various quenching conditions.

Quenching temperature (°C)	Percentage of Crystallinity(%)	Mean size of spherulite (Å)
3	95.1	6.39
25	96.4	9.38
40	97.8	9.81
45	98.9	10.96
50	100	10.52

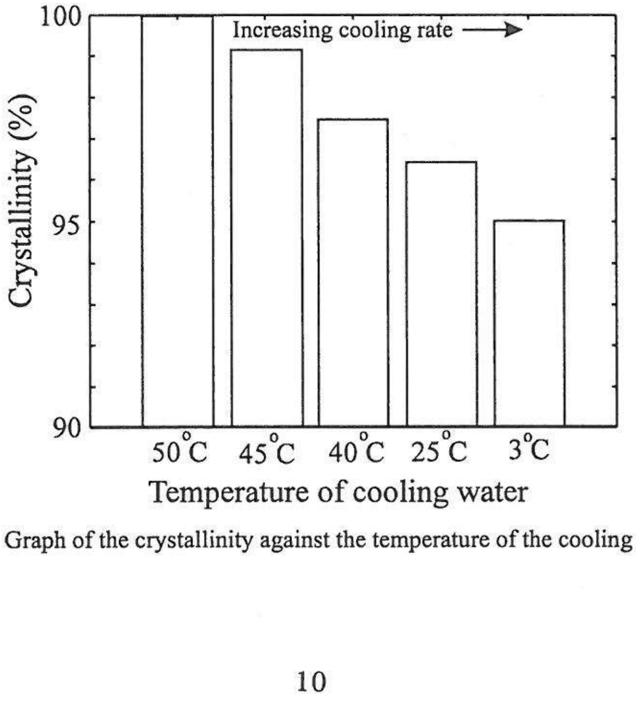

Fig. 2 Graph of the crystallinity against the temperature of the cooling water.

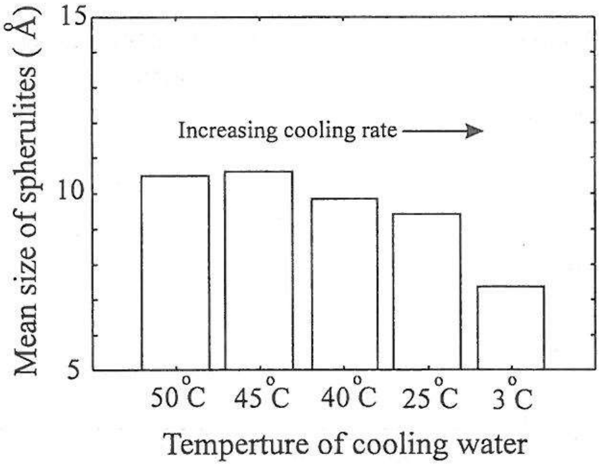

Fig. 3 Graph of the mean size of spherulites against the temperature of the cooling water.

It can be seen that the percentage of the crystallinity decreases, when the cooling rate increases. On the other hand, the decrease in the spherulite size with increasing cooling rate can be clearly recognized.

Table 2 Modulus of elasticity and impact strength at various quenching conditions.

Quenching temperature	Modulus of Elasticity (N/mm^2)	Impact strength (J/mm)
3	862	10.1
25	926	11.1
40	937	13.5
45	975	12.5
50	897	11.3

Table 2 shows the variation on the modulus of the elasticity and the impact strength at the various quenching conditions corresponding to the experimental results in Table 1. Consider the plots of the changes of the modulus of the elasticity and the impact strength with a respect to the crystallinity as shown in Fig. 4 and Fig. 5. It can be seen that, at the lower range of the percentage of the crystallinity, the magnitudes of these two properties increase as the amount of the crystallinity increases. Afterward, the magnitudes of two properties start decreasing at a certain degree of the crystallinity. This assures that both two properties does not proportionally vary only the extend of the crystallinity. Their declination can be explained as follows. When the cooling rate is low, the amount of the crystallinity is to be high whereas the size of the spherulites are large as seen in Table 1 Consequently, the large size of the spherulites causes the poor mechanical properties.

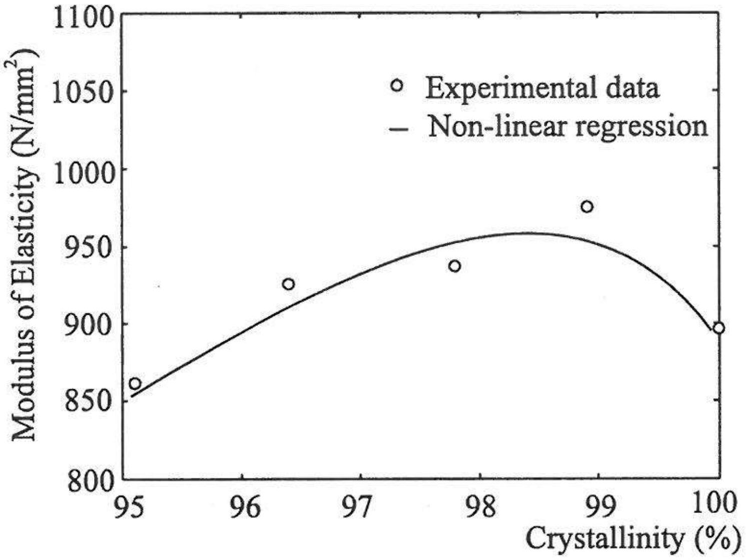

Fig. 4 Non-linear regression on the modulus of the elasticity against the crystallinity.

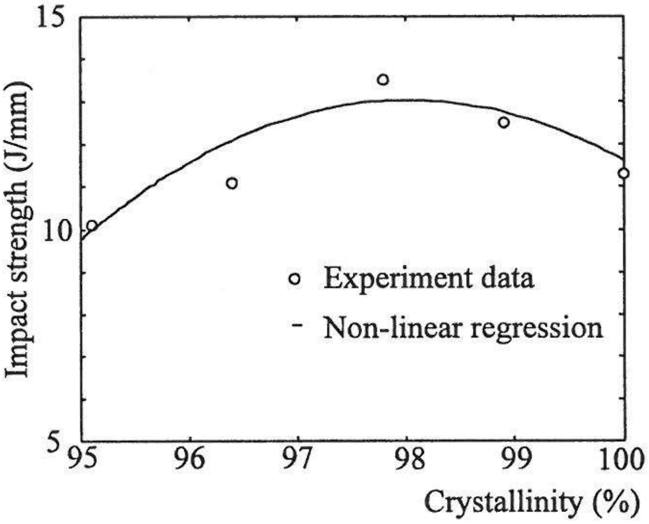

Fig. 5 Non-linear regression on the impact strength against the crystallinity.

It is noticed from Fig. 4 and Fig. 5 that the peak of two curves, that is, the modulus of the elasticity and the impact strength, takes place at different amounts of crystallinity. This implies that a given cooling condition may yield the optimal point of one property but may not yield the optimal point of other properties. Therefore, the quantitative correlation between the material structures and the mechanical properties is needed to be obtained in assessing the characteristics of the polymer processing. Next, the multi-layer feedforward neural networks are used to capture such relations of the material structures in Table 1 and the mechanical properties in Table 2. Fig. 6 and Fig. 7 show three-dimensional surface of values of two mechanical properties, which are obtained from the trained neural network with experimental data in Table 1 and Table 2. The dash line indicates roughly interpolation bases on the available data of the cooling process.

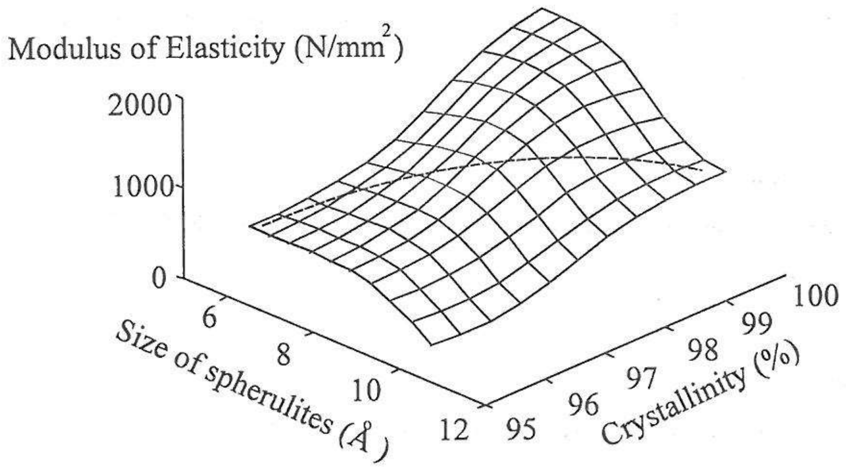

Fig. 6 Dependence of the modulus of the elasticity on the spherulite's size and the crystallinity generated by the neural networks.

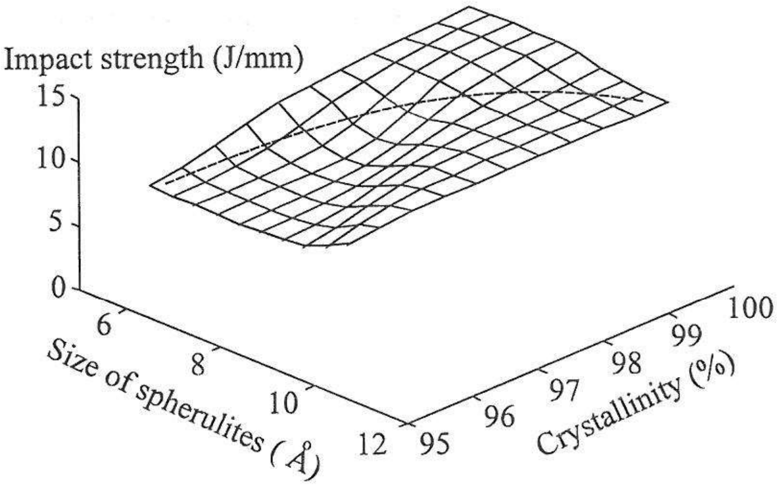

Fig. 7 Dependence of the impact strength on the spherulite's size and the crystallinity generated by the neural networks.

According to the predictive neural networks in Fig 6 and Fig 7, it can be implied that the samples with the high crystallinity and the fine spherulites may possess the good mechanical properties on the modulus of the elasticity and the impact strength. Therefore, only quenching the samples may be not enough to obtain the maximum for these two mechanical properties.

7. Conclusion

Experiments of quenching samples of HDPE at different temperatures are designed to yield the wide range of material structures, that is the crystallinity and the spherulite's size. Corresponding to those material structures as the input data, the samples are mechanically tested in order to obtain the output data for training the neural networks. Based on the observed input-output data under quiescent non-isothermal conditions, the neural networks can be used as the mathematical models, which quantitatively describe such relationship between the material structures and the mechanical properties.

8. Acknowledgement

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9. References

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